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ECUT

ENERGY CONVERSION AND UTILIZATION TECHNOLOGIES PROGRAM

Biocatalysis Research Activity

Isothermal Separation Processes

July 1982

Sponsored by:
Energy Conversion and Utilization Technology Division
Office of Energy Systems Research
U.S. Department of Energy
Through an Agreement with
National Aeronautics and Space Administration
Prepared for:
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

By:
Engineering Research West
2052 Broadway
Santa Monica, California 90404



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**Energy Conversion and Utilization Technologies Division
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The Biocatalysis Research Activity focuses on resolving the major technical barriers that impede the potential use of biologically-facilitated continuous chemical production processes.

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ISOTHERMAL SEPARATION PROCESSES

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EXECUTIVE SUMMARY

The isothermal processes of membrane separation, supercritical extraction and chromatography were examined using availability analysis. The general approach was to derive equations that identified where energy is consumed in these processes and how they compare with conventional separation methods.

These separation methods are characterized by pure work inputs, chiefly in the form of a pressure drop which supplies the required energy. Equations were derived for the energy requirement in terms of regular solution theory. This approach is believed to accurately predict the work of separation in terms of the heat of solution and the entropy of mixing. It can form the basis of a convenient calculation method for optimizing membrane and solvent properties for particular applications.

Calculations were made on the energy requirements for a membrane process separating air into its components. This, like all processes operating at equilibrium, requires operation in stages to achieve pure components. Calculations indicated that the total work requirements for a 5-stage membrane process would be about 57% that of separation by air liquefaction, and only about 2.2 times the theoretical value.

Close examination of supercritical extraction found a relatively simple thermodynamic relationship among the thermodynamic properties of the solvent, the entropy of mixing, and the heat of solution. This allows a direct estimate of the work requirements. The actual work, however, is largely due to the requirement to cycle pressure at high

levels in this method. Still, the energy requirements are very low, making up for usually high capital costs for equipment. Solution theory also gives a straightforward method of selecting supercritical extractants, especially if high selectivity is needed.

Chromatography and membrane separations can be described by either equilibrium or transfer-limited approaches, depending on the physics of the solvent-solute (-substrate) interactions. Both approaches are used in commercial applications. Care must be taken in understanding the mechanism of the separations before extrapolation or selection of improvements is made.

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TASK I. METHODOLOGY FOR ANALYSIS

A. OVERVIEW

Energy requirements for separation are generally estimated from 1) the thermodynamic work requirements, primarily from the negative of the free energy of mixing, and 2) the process heat requirements, primarily, the amount of heat required to distill, absorb/desorb, or otherwise thermally drive the separation. The former method is most often applied for gas separations, notably air separation and uranium isotope enrichment. The latter is the more common and includes hydrocarbon separations and common distillation, drying by evaporation and so forth. A more elegant method is to attempt to combine the two approaches in a thermodynamically consistent and general basis. One method is to use "availability analysis" which calculates the underlying thermodynamic work and also accounts for effects due to the application of the second law of thermodynamics to the transfer of heat in and out of a thermally-cycled process. Processes operating at temperatures different from ambient suffer losses due to incomplete heat recovery or due to a mismatch of heat capacity or pressure-volume work among streams. Separations that occur isothermally may do so away from ambient conditions. Losses attributable to such differences can be included as a primary effect depending, in most instances, on the amount of heat or expansion/compression work that is economically recoverable, and on the process temperature and pressure.

The following sections define a generalized separation process, and

derive expressions for the energy and entropy fluxes in terms of the chemical availability. The availability equation is then examined for particular types of separations possible and equations are derived for each part. Finally, equations are derived for processes operating at elevated temperature.

B. A GENERAL SEPARATION PROCESS

A generalization of a separation (or any chemical) process is shown in Figure I-1. A mixed stream of components at ambient temperature, T_0 , enters a process boundary, is subject to the application of heat and work, and exits at the same ambient temperature. The work and heat inputs are separated for convenience since processes often operate with electric power from a grid and with a separate boiler or heater. Heat, ΔH , can be supplied to the process, its "quality" determined by the entropy, ΔS . The importance of the entropy of the heat source is often not obvious but may represent a difference in energy input of 30%. Internal to the process boundaries, work could be produced, say, by a Carnot engine. This is excluded from the present analysis because it would hide some important details.

From second law considerations similar to those of heat engines, heat is exchanged with the environment. This heat is denoted by Q_0 , and, for a reversible process, is transferred at T_0 . Heat rejection (or absorption) at temperatures different from T_0 represents a loss not attributable to a reversible process and Q_0 is the minimum heat that must be transferred.

Thermodynamic work can also be added to the separation system, and is denoted by W . This is taken as a pure work term such as electricity

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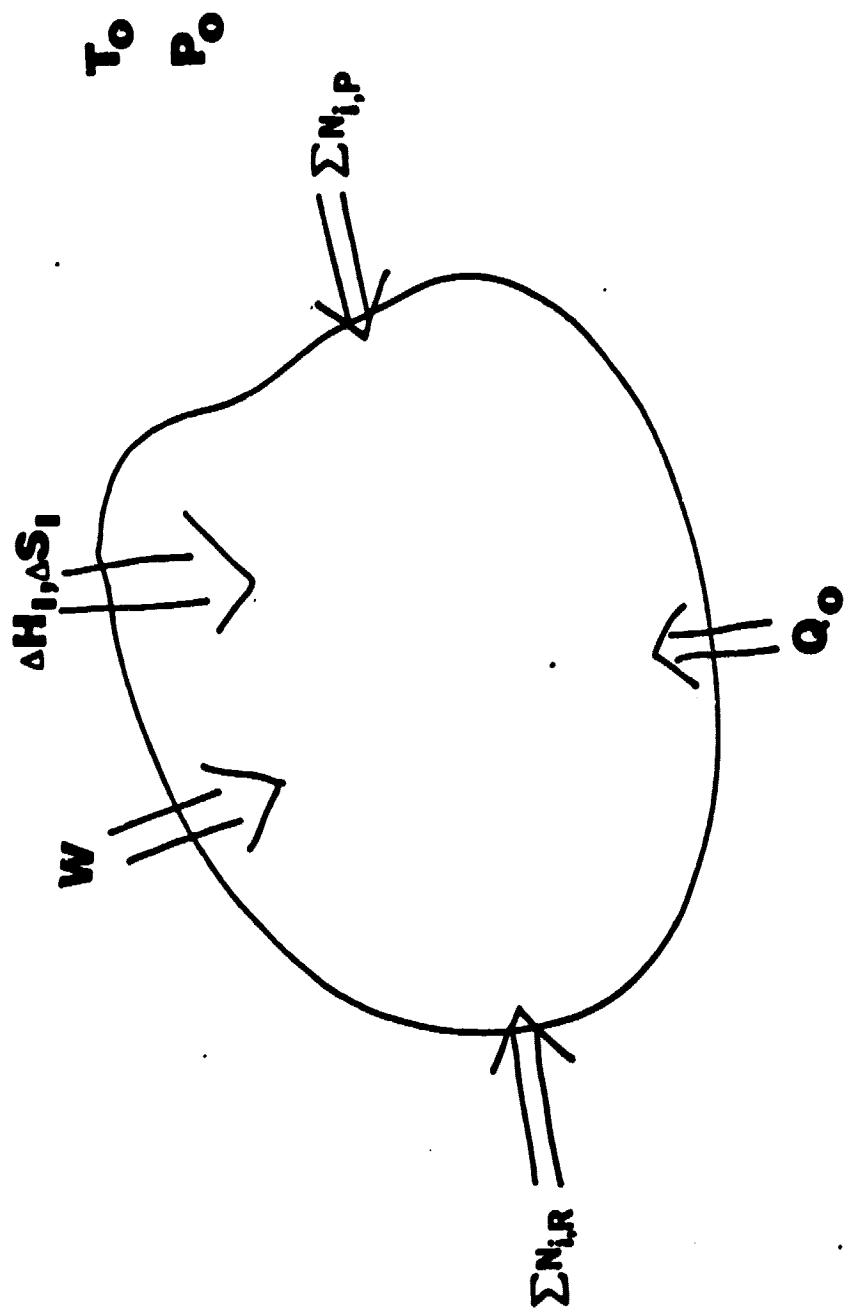


Figure I-1. General Thermodynamic Diagram of a Separation Process

or mechanical work. Chemical work is included in the thermodynamic properties of the feedstocks and products.

C. BASIC EQUATIONS

The first law balance around Figure I-1 gives

$$Q_0 + W + \Delta H_R + \sum \Delta H_{p,i} + H_1 = 0 \quad (1-1)$$

where $\Delta H_{R,i}$ refers to the "reactants", $\Delta H_{p,i}$ refers to the products, and all streams are taken as entering the process. It is unusual to write the conservation equation with all flows entering the system. It is necessary, however, due to the difficulty in keeping track of the many flows possible in chemical systems. The authors believe that this should be the general method, and will be used throughout this study.

The second law balance gives

$$Q_0/T_0 + \Delta S_R + \sum \Delta S_{p,i} + \Delta S_1 + \sum S_{irr} = 0 \quad (1-2)$$

where $\Delta S_{R,i}$ and $\Delta S_{p,i}$ refer to the entropies of the incoming and outgoing streams, respectively, and S_{irr} refers to any irreversible process that might occur in the separation process. Irreversibilities may occur from turbulence, heat dissipation, non-equilibrium separation, and from a large number of other phenomena. To maintain generality, this study largely concentrates on thermodynamically reversible systems, and the term $\sum S_{irr}$ will be taken as zero. Then, the second law balance can be written:

$$Q_0/T_0 + \Delta S_R + \sum \Delta S_{p,i} + \Delta S_I = 0 \quad (1-3)$$

The general and extremely useful "availability" equation can be derived by combining equations (I-1) and (I-3) by eliminating Q_0 to give

$$W + (\Delta H_I - T_0 \Delta S_I) + (\Delta H_R - T_0 \Delta S_R) + \sum (\Delta H_{p,i} - T_0 \Delta S_{p,i}) = 0 \quad (1-4)$$

This equation will be referred to repeatedly, primarily by evaluating the enthalpy and entropy functions for various separation processes and chemical systems.

While specific types of separations have still not been considered, it is valuable to examine several separation conditions to understand where the requirements for energy occur and, possibly, to understand where they may be controlled. It will also lead to the basis for handling increasingly more complex systems.

1. Separation at Ambient Temperature

The simplest case is when the separation occurs at T_0 , and Q_0 , ΔH_I and ΔS_I are zero. In this case, Eq.(I-4) reduces to

$$W + (\Delta H_R - T_0 \Delta S_R) + (\Delta H_{p,i} - T_0 \Delta S_{p,i}) = 0 \quad (1-5)$$

The term " $\Delta H - T_0 \Delta S$ " is very similar to the definition of the familiar Gibbs function, $\Delta H - T \Delta S$, the difference being the reference temperature. They are not interchangeable, however, since T_0 is an

external constant, and T is related to the conditions at which the enthalpy and entropy are calculated. They are, of course, identical if T_0 is the same as the reference state.

a. Ideal Mixtures

The work of separation of components is given by Eq.(I-5) as the difference of their chemical availabilities which can be calculated from knowledge of the enthalpies and entropies of the associated streams. For an ideal mixture of gases or liquids, i.e., a mixture with ideal entropy of mixing and no heat of mixing, the work required to separate the components is the negative of the work lost upon mixing:

$$W = -RT_0 \sum N_i \ln X_i \quad (I-6)$$

which is derived from Eq.(I-5) by noting that the enthalpy changes of the products and reactants are zero and that the entropy change of the products is zero, since:

$$\sum \Delta S_{p,i} = R \sum N_i \ln X_i \quad (I-7)$$

and all exit streams are considered pure. In fact, exit streams are often not pure, and Eq.(I-7) would be evaluated separately in the general case. These equations refer to the total amount of work required for separation, N_i being the total amount of material in the stream, and X_i representing the molar fraction. While N_i can be based on either weight or molar quantities, it shall be used exclusively to denote molar quantities in the remainder of this study.

Eq.(I-6) scales the minimum amount of work at ambient temperature required for separation. For air, a near-ideal mixture containing 78.1% N_2 , 20.9% O_2 , and 0.1% Ar and CO_2 , the work of separation at 25°C is 335 kcal/kg-mol of air (approximately 0.0134 kw-hr/kg of air). At \$0.065/kw-hr, this amounts to about \$21.12 per metric ton of air. The actual requirements are about 4 times the theoretical value, although commercial separation by liquefaction prepares oxygen that is only about 95% pure, an economic optimum.

b. Non-Ideal Mixtures

Mixtures may be non-ideal in the sense of having 1) an ideal entropy of mixing and a non-zero heat of mixing (Hildebrand's "regular" solutions), 2) a non-ideal entropy of mixing and a zero heat of mixing, or 3) non-ideal entropy of mixing and a non-zero heat of mixing. In the general case of (3), the thermodynamic properties of the solution or mixture must be known in sufficient detail such that the enthalpy and entropy of all streams can be calculated. The difference is then taken according to Eq.(I-5). Many common non-ideal solutions are very nearly regular solutions whose properties can be estimated by knowing only the heat of solution, ΔH_S . This is particularly true of many dilute solutions of interest in separation technology where the solute does not interact with itself, and where the solution can be said to be without long-range order. In this case, Eq.(I-5) gives:

$$W = -RT_0 \sum N_i \ln X_i + \Delta H_S \quad (I - 8)$$

where the heat of solution is just the difference between the enthalpies

of the products and reactants. The heat of solution can be estimated for regular solutions from vapor pressure data or heats of vaporization (Hildebrand, 1950), so that the theoretical energy of separation can be estimated with easily obtainable data.

c. Other Mixtures

Many of the processes of interest in this study involve delicate separation steps such as separation of racemic mixtures, separation of large biological molecules and so forth. In most cases, these separations can be occurring from regular solutions, or, for gaseous systems, from ideal solutions. Strongly bonded mixtures such as solutions of strong acids or ionic salts cannot be treated in these ways without serious error. Since these materials interact strongly with their solvents, isothermal separation methods probably could not be applied in a practical sense. For example, separation of water from 32 w/o sulfuric acid by reverse osmosis would require pressure ratios of about 3×10^{14} to overcome a heat of solution of about 13000 kcal/kg-mol. Separation of water from brine requires a pressure ratio of about 28 to overcome about 1000 kcal/kg-mol.

3. Separation at Elevated Temperature

When separation is required at temperatures other than ambient, heat must be transferred in and out of the separation process according to Eq.(I-5). The reason for heating is, in the case of separation methods under study, often to increase the solubility of components or to make them fluid. It may have the additional effect of reducing the theoretical work of separation although this is not the case for ideal solutions. Figure (I-2) shows a generalized process in which heat is

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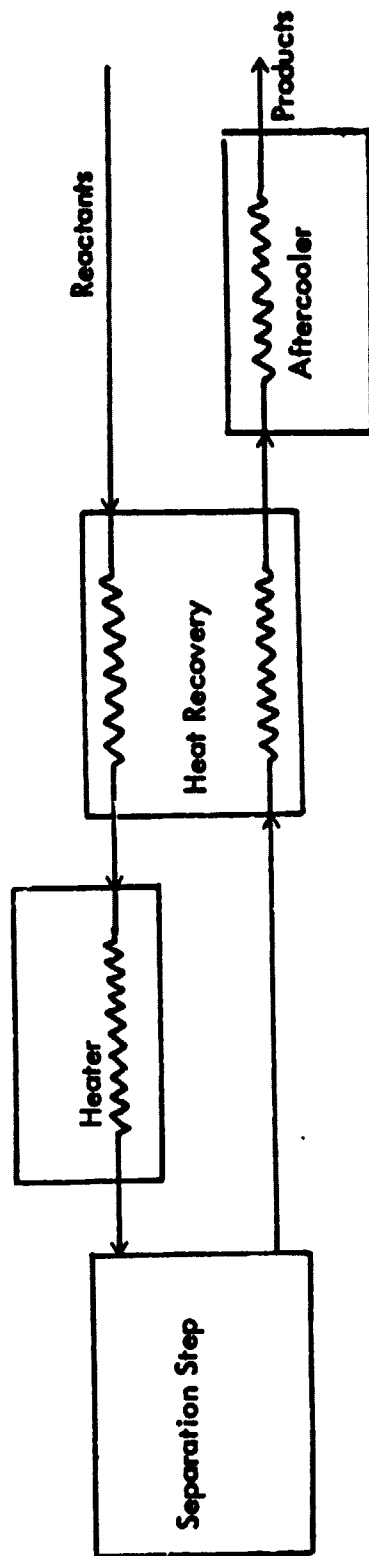


Figure I-2. Isothermal Separation at Elevated Temperature

recovered by preheating the feedstocks, and heat is rejected to the environment. Eq.(I-4) must be solved for the case in which the incoming stream is heated, the outgoing streams are cooled, and heat is supplied externally by means of a fluid. A problem for a general analysis such as this is to estimate the amount of heat recovery attributable to heat exchangers. This is somewhat arbitrary because the actual amount of heat recovery is related to the cost of energy, the cost of heat exchangers, and the temperatures at which heat is being transferred. In a reversible process, no external heat requirements are needed, an artifact that, in such a process, availability is conserved. Thus, the study must deviate from the original purpose and estimate heat recovery on an engineering basis.

a. Estimating Heat Recovery

The amount of heat recovered is dependent on the costs of energy and capital equipment, but can be described simply by the temperature, T_L , at which heat recovery is no longer profitable. This temperature depends somewhat on the industry and type of equipment utilized. Generally, however, the temperature at which heat enters cooling towers can be taken as about 78°C , representing a second law (Carnot) loss of about 15% on the usage of energy. Electric utilities would go lower, while the chemical industry would go higher. For simplification, 78°C will be taken as the practical heat rejection temperature, T_L .

b. Ideal Mixtures

As before, the simplest case is that of an ideal mixture being separated at elevated temperature, T_H . The work required for

separation is:

$$W = -RT_H \sum N_i \ln X_i \quad (1-10)$$

and the added energy requirement is approximately

$$\Delta H_1 = \sum N c_p (T_L - T_0) \quad (1-11)$$

More correctly, Eq.(I-11) should account for a small difference in heat capacities of reactants and products. This could become important, for example, if the feed contained condensible vapor which exited as a liquid. A more general expression would be

$$\Delta H_1 = \sum \Delta H_{P,i} - \sum \Delta H_R = \sum N_i c_{p,i} (T_L - T_0) \quad (1-12)$$

the latter holding rigorously only for ideal solutions.

c. Regular Solutions

Regular solutions have an ideal entropy of mixing and a non-zero heat of mixing, and the energy requirements for separation can be thought of as occurring in two parts. The work requirement to account for the entropy of mixing is given by Eq.(I-10), but the heat of mixing will generally be an irregular function of temperature. Hildebrand (1950) shows that, under a variety of assumptions following from the definition of regular solutions and other physical principles, that the total work requirement is given by

$$W = \Delta G = -RT \sum N_i \ln X_i + \frac{V_M}{2} \sum_i \sum_j A_{ij} \phi_i \phi_j \quad (1-13)$$

where V_M is the molar volume of the solution, ϕ represents the volume fractions of each component, and

$$A_{ij} = (\delta_i - \delta_j)^2 \quad (1-14)$$

where δ represents the square root of the cohesive energy density or the "solubility parameter." This function is calculated from the heat of vaporization and the molar volume by

$$\delta = \left(\frac{H_i - RT}{V_i} \right)^{1/2} \quad (1-15)$$

The solubility parameter is a relatively slowly varying function of temperature provided that materials do not change phase. Thus, increasing or decreasing temperature to aid separations does not change the thermodynamic requirements appreciably.

D. SUMMARY

Basic equations were developed for separation processes in which the work and heat requirements can be determined. Equations describe the thermodynamics of separations occurring at both ambient and elevated (or sub-ambient) temperature, and for ideal and regular solutions. Mixtures not described by these two approaches are believed, on the whole, to represent poor applications for isothermal separation processes. This is because their high heats of mixing can only be overcome by large amounts of thermal energy.

Losses associated with operation at elevated temperature were found to be independent of the reversible thermodynamics, and depend largely on the economical temperature for heat recovery. This depends on the costs of energy and capital equipment.

Elevated temperature has relatively little effect on the theoretical separation energy. This is somewhat of a surprising result since distillation processes are strongly dependent on temperature. This may be due largely to operating characteristics related to pressure rather than to temperature.

TASK II. CALCULATION AND COMPARISON OF SEPARATION WORK

A. OVERVIEW

Task I indicated the basic approach to second law analysis of separation processes operating at constant temperature. For convenience, work and heat requirements were separated, although there is no theoretical reason for this. Rather, the thermodynamic work requirements are often of more concern to difficult separation problems discussed in this study than to conventional, heat-driven methods such as distillation (even those requiring many theoretical plates) and absorption/desorption. The fundamental heat requirement was shown to be due primarily to finite heat transfer surface in processes operating at temperatures other than ambient. This heat may also be supplied by inefficient use of work such as occurs with electrochemical separation processes operating at greater than theoretical voltage.

In this task, the energy requirements will be calculated using the equations developed in Task I. Since the processes operate in equilibrium stages, methodology must also be given for stagewise calculation to obtain a given separation. This requires concurrent calculation of material balances and separation variables. These methods are presented in Appendices A and B, and the results shown in this section. Heat requirements due to off-ambient operation are not calculated. Such requirements are not needed in a thermodynamic system, and, in any case, can be calculated from knowledge of the practical heat rejection temperature, T_L , or from inefficiencies associated with the

utilization of work.

B. MEMBRANE SEPARATION

1. Concepts

The use of membranes for separations and transport of materials is extremely widespread in biological systems and is becoming important in industrial applications through the use of reverse osmosis and hollow fiber gas separation methods. Biological systems are capable of extremely subtle separations, and the biological membranes are capable of adapting continuously to aid in separations and transport. Industrial processes usually involve much larger energies and transport rates, and are designed to utilize fluid mechanics to aid in the transport of materials to and from the membrane. Despite the usual design principles in industrial applications to accelerate the separation at the expense of efficiency and thus take the separation away from equilibrium, many membrane processes still operate substantially at equilibrium if the process system is taken as occurring between the fluid dynamic boundary layers.

Figure II-1 diagrams a process in which 1) an incoming stream is placed in contact with a membrane, 2) one or more components diffuse across the membrane, and 3) products are continuously removed. The driving forces for such a separation can be a concentration gradient or a partial pressure gradient, both representing logarithmic driving forces from Eq.(I-6). Temperature gradients need not be considered since they generally cannot be maintained in high-surface apparatus needed for membrane processes. Generally, the properties of the membrane will determine which components will diffuse through and which will not.

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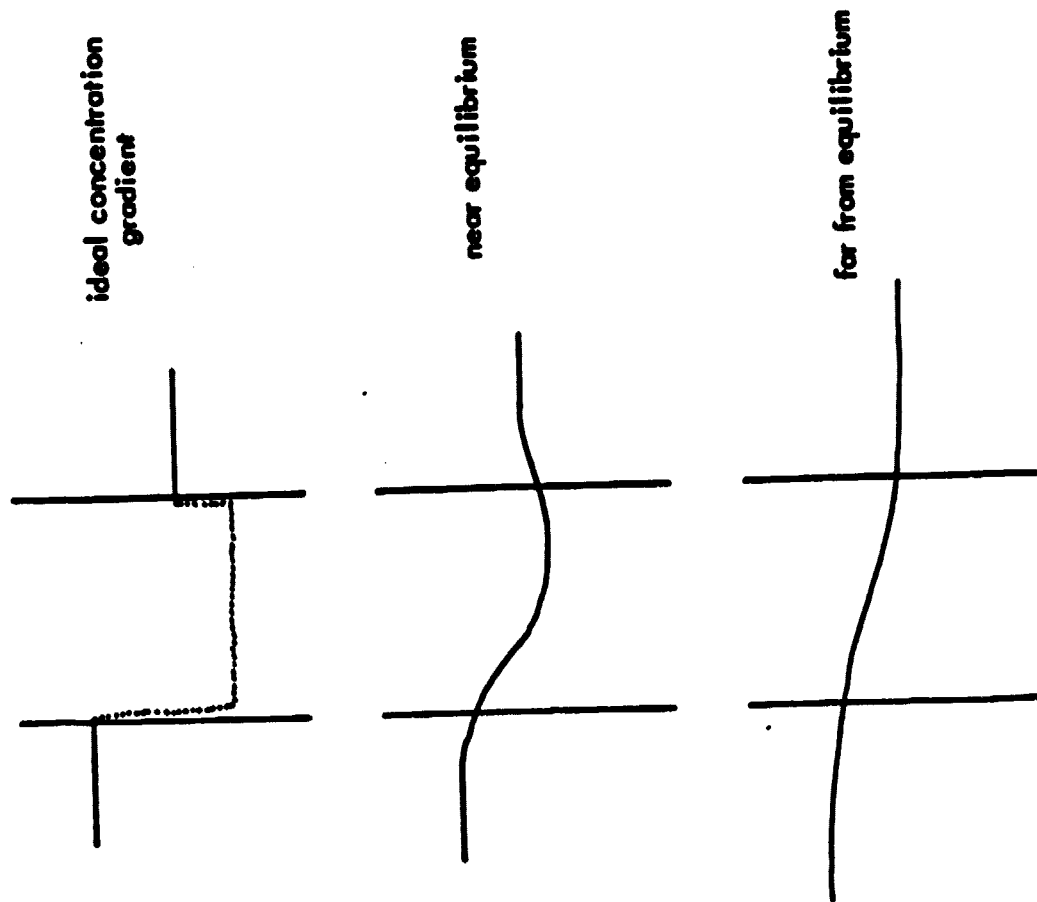


Figure II-1. Schematic Of a Membrane Separation Process

Exceptions may occur when diffusion layers are set up by the incoming stream in which case the membrane would act merely as a support. A common case of the latter is the formation of activated sludge in water treatment.

In the general case, a membrane process can be considered as two or more processes in equilibrium, although the overall process is prevented from achieving equilibrium by the membrane.

For analysis, both the reactant and product streams can be considered separately in equilibrium with the membrane, and the work requirements can be estimated, to a first approximation, by the differences in concentrations or partial pressures across the membrane. The calculations for equilibrium depend on the type of "solution" the reactants and products form with the membrane. Gaseous reactants and products can be taken, with little error, as ideal solutions or mixtures. Their interaction with the membrane, however, must be non-ideal. Otherwise, no separation could take place since the gases would absorb and desorb in the same proportion as their concentration (Raoult's law). The interaction will, in general, be irregular and not amenable to exact calculation. Many, perhaps most, of the interactions can be treated in terms of forming regular solutions according to Eq.(I-13). Systems not amenable to this method are often too energetic for separation by membranes in any case since they would involve strong chemical effects.

Similarly, liquid streams may be considered as regular solutions which form other regular solutions with the membrane, and which form regular solutions of liquids or ideal mixtures of gases when separated.

2. Separation of Gases

The preparation of a pure from a mixture of gases is the simplest and most illustrative example of membrane separation. Figure II-2 shows such a system where the driving force for separation is the difference in partial pressure of component 1 from the reactant stream to the product stream. Reference to Eq.(I-6), however, shows that, as the partial pressure of components in either phase becomes small, the separation work increases sharply. This results from the logarithmic form of the equation, and implies, as will be described, that membrane processes producing pure products are inherently staged devices.

For comparison with conventional methods, the separation of air by a membrane is analyzed. The membrane is assumed to physically absorb the components in air. Other types of membranes are possible such as acid-base systems and so forth. Again, these involve relatively energetic interactions which are difficult to reverse to effect a separation. Air is considered, for simplicity, to consist only of oxygen and nitrogen. Inclusion of minor components is straightforward, although it becomes somewhat complex in form. Calculation proceeds from the assumption that the mixture to be separated is absorbed into the membrane in amounts dictated by its partial pressure and by its non-ideal interaction with the membrane. The latter interactions can be estimated from the physical properties of the gases and of the membrane, namely, their solubility parameter, δ , and partial molal volumes. Basically, procedure is to calculate the difference in partial pressures of the gases across the membrane. This is followed by a mass balance to determine the composition of the next stage. This calculation proceeds stagewise until a separation of specified quality is achieved. Because

of the changing volumes and concentrations of gases, the area requirements for the membrane change at each stage, usually becoming smaller as the separation proceeds. The amount of area is also proportional to the partial pressure of the components for a given separation efficiency.

The enrichment depends sharply on the properties of the membrane, primarily its δ and molar volume. Figure II-3 plots the fraction of oxygen in the enriched stream of a multistage separation process using membranes of fixed partial molar volume and varying δ . The calculations are presented in Appendix A. As δ increases the relative enrichment increases. There is a dramatic reduction in gas solubility in the membrane, however, which largely negates the value of the enrichment. This is because the high separation ability must be compensated by extremely large membrane area. Figure II-4 illustrates the tradeoff based on experimental gas solubility data (Lawson, 1979) and an estimate of the diffusion rate through fluorocarbon membranes. If firm costs could be attributed to membrane area and the cost per stage, then an economic minimum could be calculated for the physical properties of the membrane.

A calculation of the work requirements was made based on the data in Appendix A and Figure II-4. The work can be approximated, although only roughly, by estimating the lost availability due to irreversible pressure drop across a 5-stage membrane process. This is done by assuming an optimum pressure drop of twice the theoretical value and calculating the work according to Eq.(I-6). The total work required is estimated at about 770 kcal/kg-mole (0.0308 kw-hr/kg) of air, about 57%

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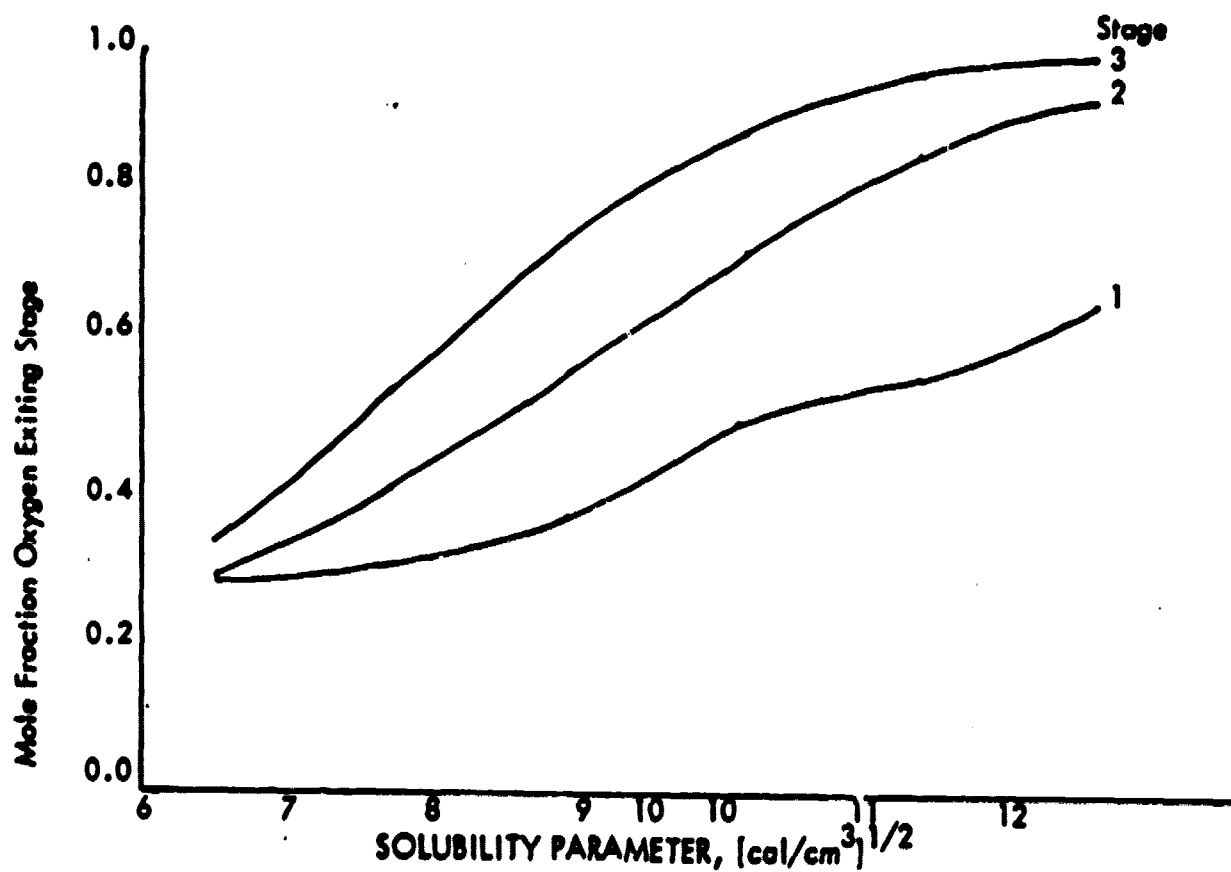


Figure II-3. Oxygen Fraction in Multistage Membrane Separation

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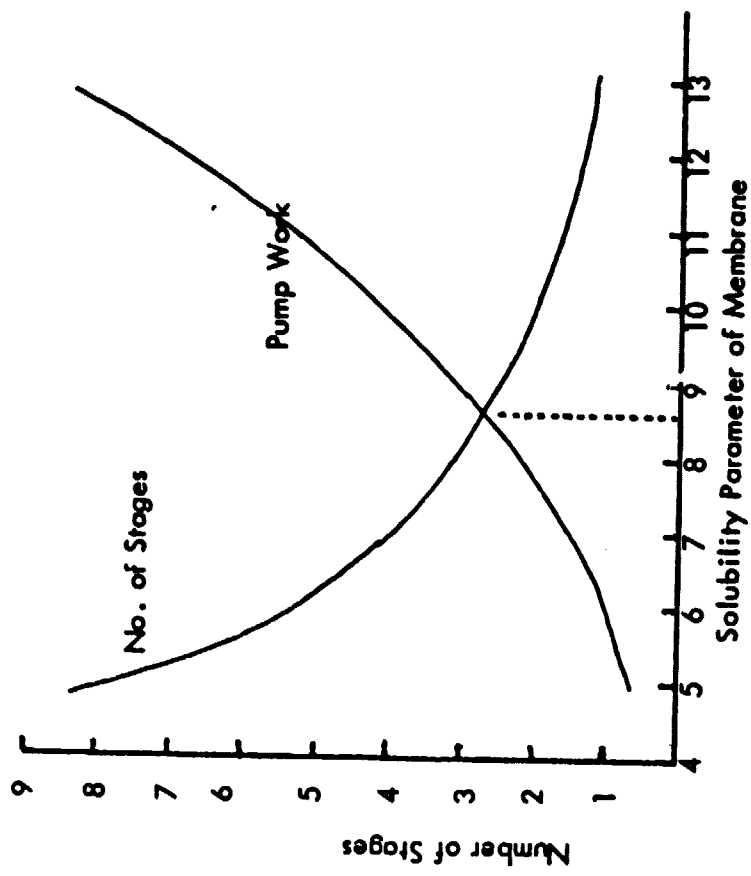


Figure II-4. Stages Required for Membrane Separations

of the amount required by liquefaction. It should be noted that the assumptions used in this calculation exclude pump/compression losses due to small tolerances in membrane systems, but compensates for them somewhat by off-equilibrium pressure ratios.

The above calculation indicates some important aspects of membrane separation of gases. Separation at near-equilibrium conditions requires multiple stages to 1) provide for finite transfer rates (good gas solubilities in the membrane), and 2) keep the pressure gradients tractable. Some gas separations operate by processes that are dominated by mass transfer rather than by equilibrium. These tend to the effusion mechanism which depends on widely different rates of diffusion through the membrane. The physics of transport are different from that of equilibrium membranes. Effusion membranes cause differences in transport rate by pore size while equilibrium membranes cause the same by varying solubility. The Prism process for separating hydrogen, recently commercialized by Monsanto, is an excellent example of a non-equilibrium membrane. Gas chromatography using zeolites is an example of an effusion separation process operating stagewise and mimicking equilibrium processes.

Restated, membrane processes for gas separations can be divided into two classes, equilibrium and effusion processes. They may be difficult to distinguish in some cases. Equilibrium processes generally require stagewise operation and will have much lower (theoretical) energy requirements. Effusion processes favor single stage operation with high transport rates. These features lead to inefficiency which can be related directly to the thermodynamic irreversibilities associated with

mass transfer occurring far from equilibrium

3. Separation of Condensed Phases

Condensed phases such as solutions of liquids or solutions of solutes in liquids present a different system from gas separations. First of all, the concentration of species is much higher due to the large difference in density between gases and liquids. Mass diffusion rates, however, are much smaller so that concentration polarization, i.e., depletion of species at the membrane boundary, may become important. A common membrane separation is reverse osmosis, a process which operates at the order of magnitude of the equilibrium osmotic pressure. The actual pressure is somewhat larger than theoretical to create finite separation rates, but the process illustrates the feasibility of running solvent/solute separations at near equilibrium conditions. Ideal and regular solution approaches do not describe the membrane chemistry. Qualitatively, however, the membrane is able to dissolve and pass water while rejecting salts. Conventional technology suggests that the blockage of salts is due to the large size of anions and cations relative to water. This can be equally treated as a complex solubility phenomenon in which the long-range order of hydrated ions prevents solubility by large, non-ideal entropy effects.

Biological systems operate a large number of membrane separations in the liquid phase at conditions very close to equilibrium. Biological separations and chemical reactions often occur with a near-zero entropy change, a fact which allows these processes to operate over a range of environmental temperatures. Separations, however, seem to be actively assisted by changes in the biological membranes as the separation

proceeds. This makes the separation capable of concentrations in excess of that calculated for single-stage membrane processes. While such separations were not examined in this study, it may be possible to model living membranes as multistep separation devices with infinite stages. The mathematics would be similar to a problem in compound interest.

C. SUPERCRITICAL EXTRACTION

1. Concepts and Thermodynamics

Supercritical extraction relies on the excellent extractive power of solvents above their critical points to achieve separations that are ordinarily difficult to achieve in practice. Figure II-4 shows a diagram of such a process in which 1) the feedstock and solvent are pressurized and, if necessary, heated, 2) the feedstock is contacted with the solvent, 3) the unextracted material and solvent/solute mixture leave the extractor where pressure is recovered, and 4) the solvent and solute are separated by flashing. In a thermodynamically reversible process, the compression work will just equal the pressure recovery. In a real system, pressure recovery can be taken as about 70% efficient.

The mechanism of supercritical extraction is unknown. From the thermodynamic point of view, however, the explanation seems clear. The addition of pressure-volume work to the solvent allows it to overcome the entropy of mixing and the heat of solution:

$$W = \int P dV = -RT \sum N_i \ln X_i + \Delta H_s \quad (II-1)$$

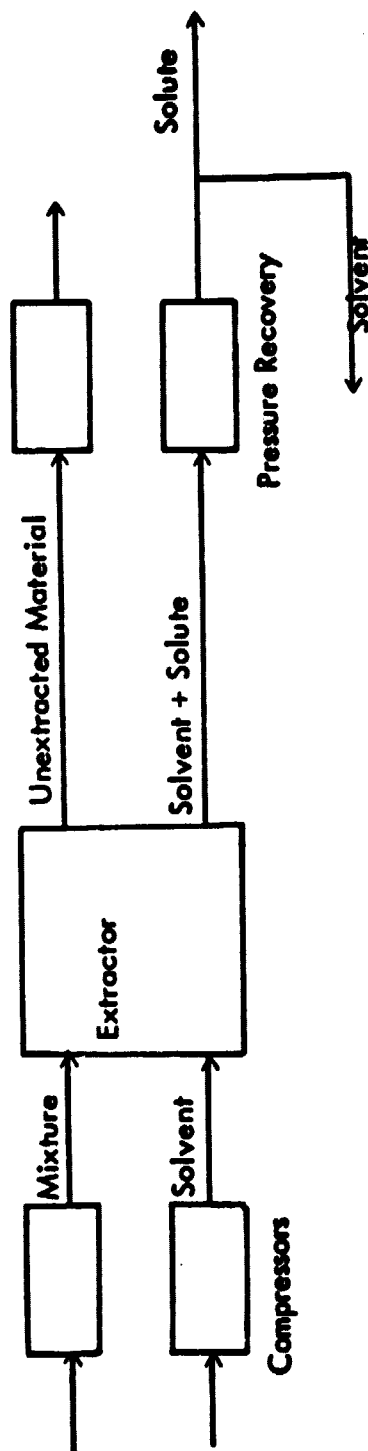


Figure II-5. Schematic of a Supercritical Extraction Process with Energy Recovery.

where ΔH_s is the heat of solution of the solute in the solvent.

Eq.(II-1) allows a surprisingly straightforward calculation of separation work, especially if the heat of solution can be estimated.

2. Extraction of Caffeine with Carbon Dioxide

For an example, the extraction of caffeine ($C_8H_{10}N_4O_2$) by carbon dioxide was examined. The calculations required an estimate of the heat of solution, and a determination of the P-V integral for carbon dioxide from ambient to its critical pressure, about 73 atm (7.66 MPa). The heat of solution is estimated by determining the solubility parameter and partial molal volume of the solute and solvent. The properties of the former, for non-volatile materials, can be estimated by additive methods (Fedors, 1974), and are easily found for the latter (see Appendix B). The heat of solution is then calculated from regular solution theory:

$$\Delta H_s = v_1 (\delta_1 - \delta_2)^2 \phi_2 \quad (II-2)$$

(Hildebrand, 1950). For caffeine in CO_2 , this amounts to about 4550 kcal/kg-mol. The P-V work is determined from the thermodynamic properties of CO_2 (Perry, 1963) and is 1995 kcal/kg-mol. From these values, Eq.(II-1) yields a mole fraction of caffeine extractable of 0.021, and an expenditure of energy equal (theoretically) to the heat of solution. The P-V work is taken as mostly recoverable. A rough estimate of the energy requirements of caffeine extraction includes a 30% loss from imperfect power recovery and the heat of solution (a minor component). This amounts to 600 kcal/kg (0.70 kw-hr/kg), or about \$0.045

worth of power. This is an attractively low number in view of the commercial price of caffeine at \$10.50/kg (Chem.Mar.Repr., 1981).

The authors have not been able to obtain plant data on extraction of caffeine, and cannot at present make a direct comparison of energy costs. Eggars (1978) discussed the thermodynamics of extraction with CO_2 by close reference to the Mollier diagram for this solvent. He estimates a phase range in temperature and pressure to use in determining the extraction and precipitation of natural products. The limits for extraction are from ambient to 87°C and from the critical pressure (73 atm) to 300 atm. If Eq.(II-1) is used, however, the Mollier diagram indicates a more restrictive area of interest, more accurately indicated by a range of temperature from 300 to 330°K , and by a small range in entropy from about 3.2 to $3.6 \text{ kcal/kg}^\circ\text{K}$. The reason is simply that this region contains the enthalpy changes required to dissolve the natural products.

3. Extractive Separation of Ethane/Ethylene

Extraction of natural products is the only way to separate these products from their substrates, and supercritical extraction is just an enhanced method of extraction. The possibility of using the supercritical extraction principle in conventional distillations allows direct comparison of thermal separation with supercritical separation. Figure II-2 shows a conceptualization of a supercritical extraction column to separate ethane from ethylene, a common and large-scale commercial problem. Conventional distillation of these two components requires sophisticated and expensive equipment because the vapor pressures of each component are very high and have about the same value.

The high-pressure distillation requires about 200 theoretical plates (Jaggars, 1974).

Figure II-2 shows how the extractive properties of CO_2 in the supercritical region would be used. Basically, the system requires maintaining a liquid phase containing primarily ethylene and ethane, and a supercritical phase containing mostly CO_2 . Liquid is pumped down the column from stage to stage, and supercritical fluid flows up the column, becoming enriched in the more soluble component. This differs in concept from a conventional distillation where the up-flowing stream becomes enriched in the component with the highest vapor pressure.

The physics of the separation methods also differs (see Table II-1). Conventional distillation operates on differences in vapor pressure which can be related to the heat of vaporization, ΔH_v , of the components. Distillation by multistage supercritical extraction operates on differences in the ratio of ΔH_v to the molar volume. Thus, when a chemical system is difficult to separate because of similarities in one property, the other may be used. In the case of ethylene and ethane, the heats of vaporization differ by only 2.1% whereas the cohesive energy densities, $\Delta H_v/V$, vary by 4.7%. This makes a large difference in the number of stages required if relatively pure components are needed. Comparative calculations are given in Table II-1. Energy consumption for supercritical extraction was estimated on the basis of 90% pressure recovery. This is easily justified since the system cycles pressure over only a small range.

D. CHROMATOGRAPHY

1. Concepts and Thermodynamics

The thermodynamics of chromatography have been extensively investigated (Purnell, 1965), first with respect to gas chromatography and later with respect to condensed phase systems. Chromatographic systems differ from other extractive separations in that three components are required: solvent (or carrier), solute, and active substrate. The substrate acts in the same manner as conventional discrete staging or flashing. The thermodynamic nature of the substrate is ambivalent. Chromatography is not described formally by equilibrium thermodynamics when conducted on zeolites or other materials utilizing pore size or other dimensional properties, for example. This is because the separation occurs solely on the basis of differences in transport properties, chiefly, the molecular diffusivity. The separation is described by equilibrium mathematics only insofar as the differences in diffusivity cause separations that mimic adsorption/desorption processes. The overall separation then looks like a long series of pseudo-equilibrium steps.

On the other hand, gas-liquid chromatography operates in equilibrium steps where the gaseous solutes absorb and desorb in a thin liquid layer distributed over the substrate. Separations of this kind can be predicted with some accuracy using methods identical to those of distillation columns.

Condensed-phase chromatography follows the same precepts. The distinction between diffusion and absorption/desorption steps is often clouded. For large molecules, stereospecific properties and other subtle differences can have major effects on the separation.

The overall energy requirements for chromatographic separations

are, however, dominated by the characteristic of these methods of requiring a large ratio of solvent to solute. Application of Eqs.(I-6) and (I-8) to the solvent and solute give the theoretical work requirements. For a typical ratio of about 10000 (perhaps 1000 on a weight basis), the term

$$RT_0 \sum X_i \ln X_i$$

per unit of species i is about 6090 kcal/kg-mol and is unrecoverable. The heat of solution is of comparable value (see Sec.II-C), leading to an overall energy consumption for chromatographic separations of between about 6000 and 10000 kcal/kg-mol.

E. SUMMARY

this study undertook analysis of isothermal separation processes utilizing membranes, supercritical extraction and chromatography. The approach was to use equilibrium thermodynamics to identify where, how, and how much energy is consumed. Following this, a comparison of energy consumption among the methods was attempted. Each method is so different in its implementation, however, that close comparisons are not possible. Partly, this is because work is expended in different ways. Membrane processes consume work by dissipation caused by forcing material through equipment with small tolerances, and by depletion of species at the surface of the membranes. Supercritical extraction processes consume work primarily from losses associated with inefficient pressure recovery. Chromatographic methods use energy largely in proportion to the amount of solvent needed to effect separation, at least for continuous and

semi-continuous processes. In each case, however, the amounts of energy, based on theoretical or semi-theoretical calculations, are low compared with conventional distillation. The reason is straightforward. These methods do not require continuous and multiple vaporizations of components with the attendant raw energy requirement and poor energy recovery, especially at lower temperatures.

To prepare pure products from equilibrium processes, the separation method must proceed stagewise. This is implied from the use of Eqs.(I-6) and (I-8) which relate the work required to the mole fraction of the material to be separated. Processes utilizing non-equilibrium principles of separation are often not conducted stagewise. An example is helium separation from natural gas which utilizes a single-step diffusion through thin inorganic membranes. These are accompanied by a large loss in availability. Their saving feature is usually simplicity and low capital expenditure.